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(56) Documents cited

**US 4107264**

**US 1501587**

(58) Field of search

**C1A**

**Selected US specifications from IPC sub-class C01G**

**(54) Recovery of titanium dioxide from ilmenite-type ores**

(57) A process for recovering titanium dioxide, useful as a white pigment, from ilmenite-type ores comprises digesting the ore with hydrofluoric acid to produce a fluoride salt-containing solution, treating the fluoride salt-containing solution with an alkali metal salt (preferably KCl) to precipitate alkali metal fluotitanate, treating the precipitate with a base to produce hydrated titanium dioxide and alkali metal fluoride, subjecting the alkali metal fluoride to electrodialytic water splitting to produce base and hydrofluoric acid, employing a portion of the base in the precipitate treating step and recycling a portion of the hydrofluoric acid to the digesting step. The hydrated titanium dioxide can be calcined to produce titanium dioxide.

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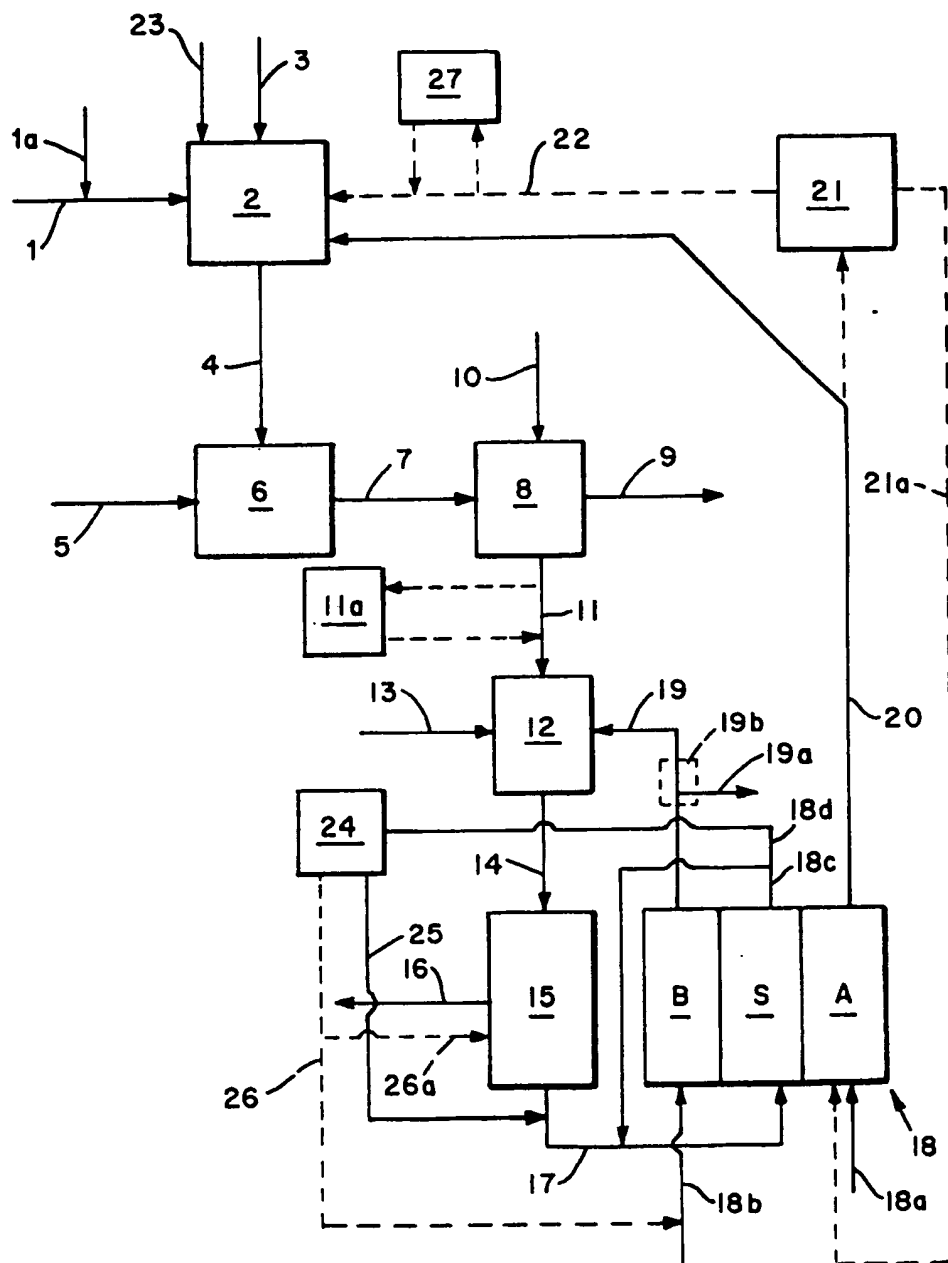


FIG. 1

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FIG. 2

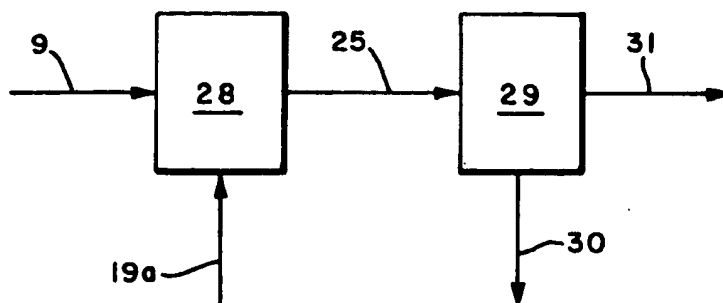
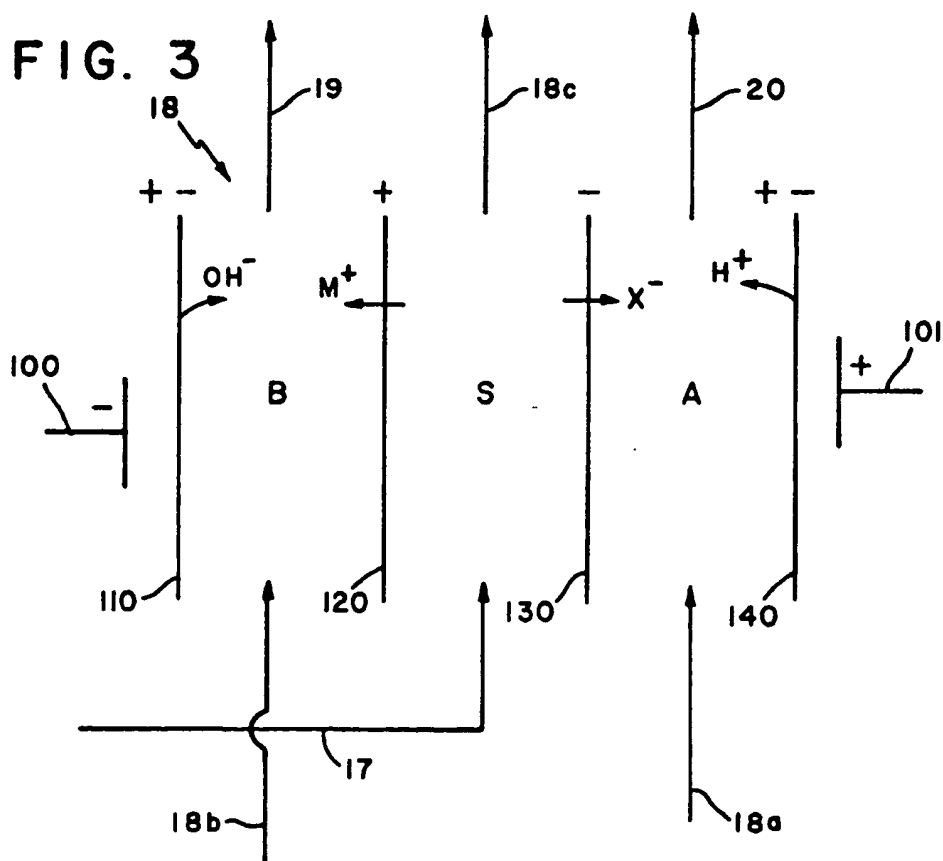


FIG. 3



## SPECIFICATION

### Recovery of titanium dioxide

#### 5 BACKGROUND OF THE INVENTION

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##### *Field of the Invention*

This invention relates to a process for recovering  $\text{TiO}_2$  from ilmenite-type ores by digesting the ore with hydrofluoric acid, and subsequently treating the product solution with alkali metal salts and a base to produce hydrated titanium dioxide which can then be calcined to yield  $\text{TiO}_2$ .

- 10 wherein the process employs electro-dialytic water splitting to regenerate the acid and base used in the digesting and treating steps. 10

##### *DESCRIPTION OF THE PRIOR ART*

- Processes for recovering  $\text{TiO}_2$  from ilmenite-type ores by digesting the ores with hydrofluoric acid or ammonium fluoride are well known in the art. 15

- U.S. Patent No. 1,501,587 (Doremus) discloses a process for producing  $\text{TiO}_2$  from ilmenite-type ores which comprises the steps of digesting the ore with aqueous hydrofluoric acid, adding a potassium compound (preferably KOH) to the digested ore to precipitate potassium fluotitanate, dissolving the potassium fluotitanate in hot water, and thereafter treating the solution with KOH to precipitate hydrated titanium dioxide which is then calcined to yield  $\text{TiO}_2$ . 20

- U.S. Patent 2,042,435 describes a process for producing  $\text{TiO}_2$  from ilmenite-type ores which comprises the steps of digesting the ore with ammonium fluoride, leaching out the titanium values with water or aqueous ammonium fluoride, and then treating the titanium values with ammonia to precipitate hydrated titanium dioxide. The by-products of ammonium fluoride and ammonia are recombined and reused in the digesting step. 25

- U.S. Patent No. 4,107,264 discloses an improved process for recovering  $\text{TiO}_2$ , useful as a white pigment, from ilmenite-type ores, including the steps of digesting the ore with aqueous hydrofluoric acid, separating out iron impurities from the resulting solution, precipitating the hydrated titanium dioxide from the iron-free solution with ammonium hydroxide, and calcining the precipitate to obtain pigmentary  $\text{TiO}_2$ , wherein the improvement comprises subjecting aqueous solutions of by-product ammonium fluoride, formed in the process, to electro-dialytic water splitting to form an aqueous solution of ammonium hydroxide and an aqueous solution of hydrogen fluoride, and recycling the aqueous ammonium hydroxide to the precipitation step and the aqueous hydrogen fluoride to the digestion step. 30

- 35 35

##### *SUMMARY OF THE INVENTION*

In accordance with this invention there is provided an improved process for producing titanium dioxide from ilmenite-type ores which includes the steps of:

- 40 a) digesting a titanium-containing ore with a solution comprising hydrogen fluoride to form a solution comprising titanium fluoride; 40  
b) treating the titanium-fluoride containing solution with an alkali metal salt to produce an alkali metal fluotitanate precipitate;  
c) reacting the alkali metal fluotitanate precipitate with a base to yield a solid comprising hydrated titanium dioxide and a product solution comprising alkali metal fluoride; 45  
d) separating the solid from the product solution; 45  
e) subjecting the product solution to electro-dialytic water splitting to produce base and aqueous hydrogen fluoride;  
f) recycling at least a portion of the base to the reacting step; and,  
g) recycling at least a portion of the aqueous hydrogen fluoride to the digesting step. 50  
50 The hydrated titanium dioxide can then be treated by any conventional technique, such as calcining, to yield titanium dioxide. 50

##### *BRIEF DESCRIPTION OF THE DRAWINGS*

- Figure 1 illustrates a schematic flow diagram of the process of the present invention including a variety of preferred, but optional, additional features. 55

Figure 2 illustrates a schematic flow diagram of one embodiment of the invention in which the effluent from the salt treatment step is converted to useful products.

- Figure 3 illustrates a schematic diagram of a three-compartment electro-dialytic water splitter employed in the process of the present invention. 60

##### *DETAILED DESCRIPTION OF THE INVENTION*

- The present invention is directed to the recovery of  $\text{TiO}_2$  from ilmenite-type ores. Ilmenite-type ores are titanium-based ores which principally comprise titanium oxide and iron (ferrous and/or ferric) oxide. The amount of titanium oxide in the ore can vary from between about 25% to about 95% by weight. Typically, ilmenite-type ore will have the following composition (by 65

weight):

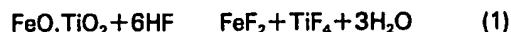
|    |                 |       |    |
|----|-----------------|-------|----|
|    | titanium oxide  | ≈ 54% |    |
|    | ferrous oxide   | ≈ 17% |    |
| 5  | ferric oxide    | ≈ 19% | 5  |
|    | silica          | ≈ 4%  |    |
|    | calcium oxide   | ≈ 1%  |    |
|    | magnesium oxide | ≈ 1%  |    |
|    | alumina         | ≈ 1%  |    |
| 10 | zirconia        | ≈ 1%  | 10 |

Other forms of ilmenite-type ores include heavy metals in place of or in addition to iron, such as nickel and chromium.

Referring to Fig. 1, an ilmenite-type ore is supplied through line 1 to a reaction vessel 2.

- 15 Optionally, the ilmenite-type ore may be modified with silica by adding silica to the ilmenite ore (via line 1a) in amounts between about 5% and about 15% by weight to form a silica-modified- $\text{TiO}_2$  product. 15

- In the reaction (digester) vessel 2, aqueous hydrogen fluoride (HF) is added to the ore via line 22. From line 3, make-up HF may be added, if necessary. The concentration of HF in the solution added to the reaction vessel can vary from between about 5% to about 70% by weight. The reaction is carried out at any temperature between about ambient and about the boiling point of the solution, but preferably is carried out at between about 50°C to about 95°C, and more preferably at temperatures approaching 95°C. Because it is preferable to carry out the reaction at higher temperatures, it is preferable to introduce an aqueous HF solution which has an HF concentration of between about 10% and about 50% by weight, and more preferably between about 20% and about 50% by weight. Higher concentrations of HF in the solution assist in raising the reaction temperature in the vessel because of the exothermic nature of the reaction. Preferably, a reducing agent, for example scrap iron, may be added to the vessel 2 via line 23 to reduce any ferric salts in the ore to ferrous salts. When iron is present in the ore, the production of ferrous salts is more preferable in the process because there is a reduced possibility of forming iron complexes during the salt treatment step described hereinbelow when the iron exists as  $\text{Fe}^{+2}$ . An example of the reaction in the digester 2 is illustrated below: 20 25 30



- 35 The resultant fluoride solution from the reaction vessel 2 is removed via line 4 for supply into reaction vessel 6. 35

- To the resultant fluoride solution in vessel 6 is added an alkali metal salt via line 5. The salt is preferably a chloride or sulfate salt of potassium or sodium, with potassium salts being more preferred, and potassium chloride being the most preferred salt. The salt may be added as an aqueous solution or in solid form. Most preferably, commercial grade potash is employed. The salt is employed to precipitate from the fluoride solution alkali fluotitanate. An example of the reaction in vessel 6 is indicated below: 40



- 45 The precipitate and the resultant product solution from vessel 6 is then fed to a filtering unit 8 via line 7. 45

- The filtering unit 8, for example a conventional rotary filter or a conventional filter press, is employed to separate the precipitate from the aqueous salt solution. The aqueous salt solution is removed via line 9 for disposal and/or further treatment as described, for example, by reference to Fig. 2 or by conventional means. The precipitate may optionally be washed with water supplied via line 10 to further purify the precipitate. The precipitate is then supplied via line 11 to a base reaction vessel 12. 50

- Prior to supply to the reaction vessel 12, the precipitate from filtering unit 8 may optionally be supplied to vessel 11a for treatment with hot ( $>70^\circ\text{C}$ ) water in an effort to reduce the content of certain constituents such as Fe, Cr, Ni, Zr, and Si. However, the preferred treatment employed to reduce the residual content of those constituents which may affect the color and/or quality of the  $\text{TiO}_2 \cdot 2\text{H}_2\text{O}$  formed in the subsequent base treatment step, such as Fe, Cr and Ni, is treatment with an organic extractant as described in U.S. 4,168,297. 55 60

- To the alkali metal fluotitanate-containing precipitate in base reaction vessel 12 is added base via line 19. Additional base, if necessary, can be added via line 13. The fluotitanate in reaction vessel 12 reacts with the base to produce hydrated  $\text{TiO}_2$  and an aqueous fluoride salt solution. While any base may be employed in the reaction, it is preferred to employ one or more of KOH, NaOH, or  $\text{NH}_4\text{OH}$ . More preferably, the base is the base of the alkali metal employed in the alkali 65

metal salt reaction, and most preferably the base is KOH. The base is preferably added as an aqueous solution in a concentration of base which can vary from between 2% to about 45% by weight. Most preferably, base concentration in the aqueous solution is between about 5 and about 20% by weight. The preferred concentration assists in better control of the volumes of material to be processed. An example of the reaction is illustrated below:



The product, hydrated  $\text{TiO}_2$  and aqueous salt solution, is then fed to a filtering unit 15 via line 14.

In filtering unit 15, the hydrated  $\text{TiO}_2$  is separated from the aqueous salt solution and removed via line 16. The hydrated  $\text{TiO}_2$  can then be processed by conventional means such as calcining to yield the final product,  $\text{TiO}_2$ . The aqueous salt solution from the filtering unit 15 is fed to an electrodialytic water splitter 18 via line 17.

The electrodialytic water splitter 18 is a three-compartment water splitter of a design as illustrated in Fig. 3. As shown, the three-compartment electrodialytic water splitter comprises a cathode 100 and an anode 101 between which are provided a plurality of membranes defining base (B), salt (S), and acid (A) compartments in sequence. Fig. 3 illustrates only one unit cell but it should be understood that any number of such cells may be employed. The aqueous salt solution is fed via line 17 into salt compartment S. Into base compartment B and acid compartment A, water is fed via lines 18b and 18a, respectively. Optionally, any of a variety of suitable electrolytes may be added to the water, for example, HF for supply to the acid compartment A and KOH for supply to the base compartment B are most preferable. When direct current is supplied to the electrodialytic water splitter, the salt in salt compartment S is split into  $\text{M}^+$  ions (alkali metal or  $\text{NH}_4^+$ ) and  $\text{F}^-$  ions. The  $\text{M}^+$  ions migrate through cation permeable membrane 120 into base compartment B and the  $\text{F}^-$  ions migrate through anion permeable membrane 130 into acid compartment A. In base compartment B,  $\text{OH}^-$  ions migrate from bipolar membrane 110 into the compartment and combine with  $\text{M}^+$  ions to form base, MOH. In acid compartment A,  $\text{H}^+$  ions migrate from bipolar membrane 140 into acid compartment A and combine with  $\text{F}^-$  ions to produce acid, HF. The base, preferably KOH, is removed via line 19 for supply of at least a portion thereof to reaction vessel 12 wherein the base treatment step occurs. The acid is removed via line 20 for further optional concentration and subsequent recycling to the digestion step as further described hereinafter. A portion of the depleted salt solution from salt compartment S can be recycled via line 18c to line 17 for further processing in the salt compartment S. The remainder of the depleted salt solution is preferably introduced via line 18d into an electrodialysis concentrator apparatus (or reverse osmosis unit) 24 to produce a very dilute fluoride solution and a concentrated fluoride solution, the concentrated solution being recycled via line 25 to the salt compartment S or more preferably to the reaction vessel 12 and the dilute fluoride solution being optionally recycled via line 26 to the base compartment B (or preferably added via line 26a as a wash for the precipitate in the filter unit 15). The monopolar and bipolar membranes employed in the three-compartment electrodialytic water splitter illustrated in Fig. 3 are well known in the art. Typical membranes employed in the apparatus described above are disclosed for example in U.S. 4,107,015, with the preferred bipolar membranes being those described in U.S. 4,116,889.

A portion of the aqueous base sufficient for the base treatment step is removed from the electrodialytic water splitter 18 (typically about 5% to about 20% by weight base) via line 19 and is supplied to the reaction vessel 12. Excess base, if any, from the water splitter may be recycled via line 19a to the base compartment B, or may be removed and employed in some other operation or sold. If, for example,  $\text{NH}_4\text{OH}$  is employed as the base added to reaction vessel 12, the aqueous base from the water splitter 18, comprising  $\text{NH}_4\text{OH}$  and KOH, may be heated via heater 19b to volatilize the  $\text{NH}_4\text{OH}$ . The gaseous ammonia product from the volatilization step can be recycled via line 19 to the base treatment step and the remaining KOH can be removed from the process via line 19a and offered for sale.

At least a portion of the aqueous acid removed from the water splitter (typically about 5% to about 15% by weight HF) via line 20 is fed directly to the digester 2 or, optionally, to the digester 2 through a concentrator 21 when the desired concentration has not been achieved in the electrodialytic water splitter. The concentrator, preferably an electrodialysis apparatus, is employed to further concentrate the acid prior to supplying the acid to the digesting step via line 22. Moreover, when the concentrator is employed, it is preferable to recycle the depleted acid solution to the acid compartment A of the electrodialytic water splitter (via line 21a). Further concentration of the acid from the concentrator may be achieved by employing a distilling unit 27 in the line 22 to further concentrate the acid prior to supplying the acid to the digester 2.

Fig. 2 illustrates an embodiment of the invention in which the effluent salt solution removed from the filtering unit 8 is treated to produce useful products which may be recycled in the process. Typically and preferably, the effluent is a soluble ferrous chloride solution. As shown,

the solution is fed to a reaction vessel 28 to which is added base via line 19a which has been removed from the electrodialytic water splitter. The base reacts with the salt solution to precipitate the heavy metal (Fe) as heavy metal hydroxide and produce a soluble salt such as KCl. The precipitate and soluble salt are then fed to a filtering unit 29 of the type, for example, employed as filter 8. Filtering unit 29 separates the iron hydroxide from the soluble KCl solution. The iron hydroxide may then be removed via line 30 and supplied to convention apparatus to be thermally processed to produce iron oxide which can may be sold or used in some other operation. The aqueous KCl can then be forwarded via line 31 to the salt treatment step. This embodiment essentially closes the system in an attempt to produce essentially only salable products and recyclable reaction constituents (which would substantially reduce the need for additional reactants).

Having described in detail applicants preferred embodiments, the following example illustrate the operation of the process described hereinabove, excluding, however, the electrodialytic water splitting step.

#### Example 1

The recovery of  $\text{TiO}_2$  was performed by forming a  $\text{K}_2\text{TiF}_6$  intermediate from ilmenite ore. 15.2 g of ilmenite ore (0.1 mole) was dissolved in 28 g of 49% HF (0.67 mole) and stirred overnight at room temperature. Most of the black ilmenite particles appeared to dissolve. There was a considerable amount of light brown material in suspension. 25 ml of water was added to the mixture and the mixture was heated to between 90–100°C for 4 hours. No change was noted in the solution. The mixture was poured through coarse filter paper which retained the brown precipitate and gave a filtrate of 35 ml of brownish-green solution. A solution of 15 g of KCl and 45 ml of  $\text{H}_2\text{O}$  was added to the filtrate causing the precipitation of a voluminous white solid. An additional 50 ml of  $\text{H}_2\text{O}$  was added to aid in mixing. The precipitate was filtered rapidly (under vacuum using No. 41 paper) and retained very little liquid. The cake was washed with 20 ml of  $\text{H}_2\text{O}$ , compacted and washed with an additional 10 ml of  $\text{H}_2\text{O}$ . The filtrate was a bright yellow green color and the cake was snow white. The solid was dried at 55°C for 2 hours. The cake (14.9 g) was then suspended in 50 ml of  $\text{H}_2\text{O}$ . 2M KOH solution was then added to the cake. After the first 50 ml was added, the mixture was highly alkaline. The mixture was then heated to about 60°C and became neutral in less than about 5 minutes. A second 50 ml of KOH was then added to the solution. The pH became neutral in less than 5 minutes at 60°C. A third addition of 20 ml of KOH was added and the pH again returned to neutral after 5 minutes at 60°C. Finally, 10 ml of KOH solution was added and the pH remained high after 5 minutes at 65–70°C. The mixture was filtered (using No. 41 paper under vacuum). Filtration was fairly rapid. The cake was rinsed with 20 ml of  $\text{H}_2\text{O}$ . The precipitate was collected and dried at 110°C overnight to yield 6.4 g of pure white solid. The recovery of  $\text{TiO}_2$  was 80% based upon the weight of ilmenite charge. The weight loss was probably due to the initial filtration step where no attempt was made to ensure complete recovery.

While applicants have fully described their invention in detail with respect to the most preferred embodiments, it will be apparent to those of ordinary skill in the art that variety of modifications, changes, additions or deletions may be made without departing from the scope of applicants' invention as defined by the appended claims.

#### CLAIMS

1. A process for recovering titanium dioxide from a titanium-containing ore, which process comprises:
  - a) digesting the titanium-containing ore with a solution comprising hydrogen fluoride to form a solution comprising titanium fluoride;
  - b) treating the titanium-fluoride containing solution with an alkali metal salt to precipitate an alkali metal fluotitanate;
  - c) reacting the alkali metal fluotitanate precipitate with a base to yield a solid comprising hydrated titanium dioxide and a solution comprising alkali metal fluoride;
  - d) separating the solid from the solution;
  - e) subjecting the solution to electrodialytic water splitting to produce base and aqueous hydrogen fluoride;
  - f) recycling at least a portion of the base to the reacting step c); and,
  - g) recycling at least a portion of the aqueous hydrogen fluoride to the digesting step a).
2. A process according to claim 1 wherein the alkali metal salt is KCl.
3. A process according to claim 1 or 2 wherein the base is an alkali metal base.
4. A process according to claim 3 wherein the base is KOH.
5. A process according to any one of the preceding claims wherein the HF concentration in step a) is between 5% and 70% by weight HF.
6. A process according to claim 5 wherein the HF concentration is between 10 and 50% by weight HF.

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7. A process according to any one of the preceding claims wherein step a) is carried out at a temperature between 50°C and 95°C.
8. A process according to any one of the preceding claims wherein the titanium-containing ore comprises titanium oxide and iron oxide.
- 5 9. A process according to claim 8 comprising the further step of adding a reducing agent to the digestion step so that substantially all of the iron oxide is in the form of ferrous oxide. 5
10. A process according to any one of the preceding claims wherein the base is used in step c) in the form of an aqueous solution containing between 5% and 20% by weight of base.
11. A process according to claim 1 substantially as described with reference to the Example.
- 10 12. A process according to claim 1 substantially as described with reference to Fig. 1 of the accompanying drawings. 10